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THE EFFECT OF GRAPHITE COMPOSITION ON POLYANILINE FILM PERFORMANCE FOR FORMALIN GAS SENSOR

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ABSTRACT. The invention of formalin gas sensors based on polyaniline (PANI) has been developed which arranged by PANI/graphite composite form. The reaction between amine and formaldehyde produced a Schiff base that alters the resistance of PANI film as a function of formaldehyde concentration. The response of the sensor was measured in variations of graphite composition with 3%, 10%, and 25%. The results showed similar patterns in all concentrations of formalin. However, the sensor response at 10% and 25% graphite decreased dramatically. The formalin with concentration 400 ppm shown the response with 3% graphite was 1.62 times greater than 25%. Addition of too much graphite makes the absorption area on the PANI surface becomes less because the graphite covered it. In this case, the sensor performance was still stable and functional, but the measured resistance seems smaller because the sensor conductivity level more dominated by graphite. Therefore, composites of polyaniline and graphite can be used as sensors to detect the presence of formaldehyde gas.

KEY WORDS: Formalin, Graphite, Polyaniline, Resistance, Sensors

INTRODUCTION

For determination of the formaldehyde content has been done, among others, by using spectroscopy, voltammetry, and gas chromatography (GC). This method was relatively selective and sensitive, however it required long analysis time, involved a lot of reagents, and is not economical because the price is prohibitive [1]. In Indonesia, tumeric paper was one of the natural alternative material had been developed for detecting the presence of formalin, the detection method was quite economical but not accurate because the detection level only functions like control of the presence or absence of formalin (positive and negative) [2]. So, it is necessary to innovate formalin detectors that are fast, cheap, and simple, but accurate, so that the public can utilize them.

The use of polyaniline-based gas sensors (PANI) has been widely developed. For example, the application of the PANI gas sensor to detect the presence of carboxylic acids in fruits such as apples and strawberries, which have found detection limit below 0.62 ppm [3]. Furthermore, the fabrication of colloid-based PANI sensors has been carried out to detect the presence of ammonia gas (NH₃), PANI was synthesized in xylene and chloroform through a surfactant medium. The detection limit obtained around 100 ppb to 10 ppm [4]. Then, the same research related to the application of PANI as an ammonia gas sensor was also carried out by [5]; namely, PANI polymerization carried out on the graphene surface with a hybrid system.

Therefore, in this study, a composition of graphite was carried out to determine the effectiveness of the performance of PANI/graphite sensors.

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EXPERIMENTAL

Tools and materials

The equipment used in this study includes general glass equipment, analytical weighing balance, magnetic stirrer, Buchner funnel and vacuum pump, vacuum oven, mortar and pestle, ultrasonic bath, pellet making equipment, autoclave, oven heater, Avometer, and airbrush sprayer. The materials used in this study were aniline (Merck), ammonium persulfate/APS (Merck), hydrochloric acid (HCl) 1 M and 37% (w/w), aqua dm, technical acetone, DMSO (dimethyl sulfoxide), formaldehyde (Merck) and Whatman filter paper No. 42.

Synthesis of polyaniline/graphite composite

A total of 3.72 g of aniline ($\rho = 1.022 \text{ g mL}^{-1}$) was dissolved in 1 M HCl solution. The second solution was made from 11.92 g APS (ammonium persulfate) which was dissolved in aqua demineralization. Before being mixed, the two solutions were sonicated for approximately 30 s to obtain the perfect dissolution of the substance. After that the two solutions are mixed with graphite (with variations of 3%, 10%, and 25%), then shake for a while then the polymerization was allowed to last 5 °C without stirring for one day (24 h).

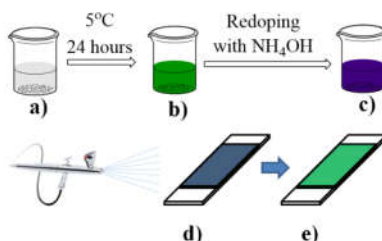


Figure 1. Stage of PANI polymerization and film making.

The green precipitate formed known as PANI-ES (Polyaniline Emeraldine Salt). Then, the slurry was filtered using Buchner, which connected to a vacuum pump to obtain PANI-ES precipitate. Furthermore, the precipitate obtained was rinsed with acetone, to remove the oligomers which were still attached to the polymer surface. Then, doping was done again using 1 M HCl and dried in an oven 50 °C for 24 h. Then, dedoped using NH₄OH 1 M for 3 h until PANI-EB (Polyaniline Emeraldine Base) obtained [6, 7].

Fabrication of polyaniline thin films

The preparation of PANI/graphite films was carried out by dissolving PANI-EB in DMSO (dimethyl sulfoxide) and then put in a bottle of water brush sprayer. A thin film of polyaniline was made on glass with a film area of 1 cm x 1 cm heated over a hotplate at 160 °C. PANI solution was sprayed slowly until the golden-dark polyaniline film was obtained. Then, the PANI-EB thin film was reshaped with 1 M HCl solution [8, 9].

Sensor performance testing

The sensor was tested using an Avometer measured based on changes in resistance for 210 minutes. Formalin at various concentrations was injected into vacuum containers to measure the

effectiveness of sensor performance that obtained by measuring the initial resistance (R_0) and Resistance (R).

RESULTS AND DISCUSSION

Synthesis polyaniline/graphite

Polyaniline was synthesized based on rapid mixed method in acidic-aqueous media, where aniline and APS was mixed quickly together (Figure 1). The synthesis process was carried out in a temperature of 5 °C, this is because that the aniline polymerization process was an exothermic reaction, so a cold medium was needed to make slow reaction and produced an excellent polymeric structure [10]. This method has several advantages compared to other methods, which can be done on a large scale with the results of PANI-ES green powder, then this product was easily separated so that it was more flexible to use in the process of modification and application [11]. Subsequently, PANI-ES was carried out by developing using an ammonium base to obtain PANI-EB.

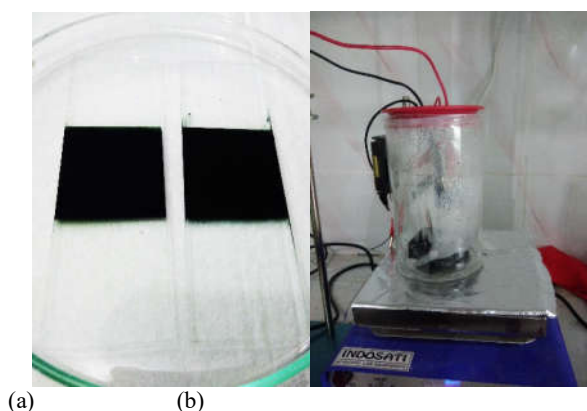


Figure 2. The PANI/graphite film (a) made by the airbrush spray technique and (b) the sensor performance testing process.

Raman characterization of polyaniline synthesis

The band around 1495 cm^{-1} associated with the $\nu(\text{C}=\text{N})$ stretching modes of semiquinoid units. This band increased on the PANI EB form, and this was caused by the quinoid ring on ES being stabilized by polaron, so the structure of $\text{C}=\text{N}$ was not very observed. Besides, in the band at 1188 cm^{-1} seen almost happened peak separation, this area is the vibration of $\nu(\text{C}-\text{H})$ benzenoid. The band at 1212 and 1166 cm^{-1} was a vibration of $\nu(\text{N}=\text{Q}=\text{N})$ and $\nu(\text{C}-\text{H})$ on the benzenoid ring [12]. Stretching $\nu(\text{C}-\text{N})$ both from the secondary amine group, imine, protonated amine and amine with the polar lattice were observed in the $1200\text{--}1495\text{ cm}^{-1}$ area. The most exciting thing was the rise of the peak at 1495 cm^{-1} in the loss protonation condition. This vibrational mode appears as stretching of $\nu(\text{C}=\text{N})$ on the quinoid ring. Also, stretching $\nu(\text{C}=\text{N})$ appears with reasonably high intensity in the form of pernigraniline. Therefore, this information is sufficient to confirm that the PANI appeared on base form [12]. The band at 416 cm^{-1} was assigned a torque change of $\nu(\text{C}-\text{N}-\text{C})$ which directly regulated the conformational changes of the quinonoid ring to form a semi quinonoid ring. Therefore, it was assumed that this torque intensity affects the vibrations strongly at 1192 and 1620 cm^{-1} [13].

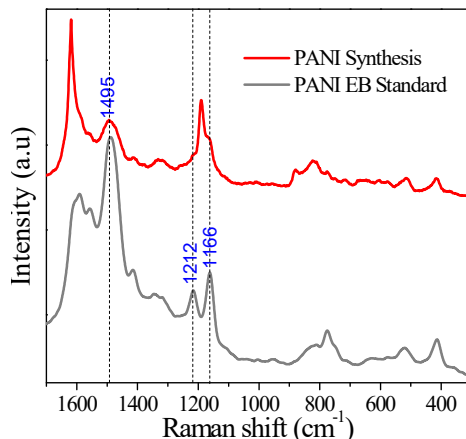


Figure 3. The Raman spectra (excitation wavelength 488 nm) of PANI synthesis and EB standard.

Fabrication polyaniline/graphite film

The fabrication of PANI/Graphite film was done by airbrush spray technique on the heated substrate according to the boiling point of the solvent. Figure 2 shows the PANI film. It is known that the PANI in the EB form has better solubility than salt form so that in making films, PANI-EB was first dissolved into DMSO [4, 13]. After the film was formed, PANI-EB in the film was re-doped with HCl 1 M solution to obtain PANI-ES.

Effects of variations in graphite composition on polyaniline/graphite composites

The measurements of sensor responses in PANI/Graphite composites have been determined with various additional graphite compositions. The sensor response increases when injected with formalin, then decreases to near its original value when cleaned with air. The increase in resistance when exposed to formaldehyde was caused by aldehydes, which react with amines to form the Schiff base [14]. The Schiff base deprotonates PANI and increases resistance. Besides, signal recovery observed during cleaning with air was caused by the desorption of water from the PANI film (Figure 4).

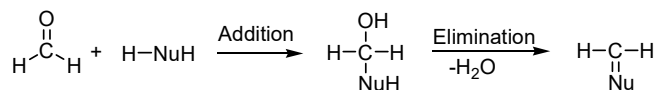


Figure 4. Mechanism of formation of Schiff bases, nucleophilic addition reaction of formaldehyde.

Figure 5 shows the process of sensor performance at various formalin concentrations. The increase of resistance was a function of formalin concentration. This can be seen in all three curves, which shown an increase in resistance when injection of formalin. But on the other hand, there was a decrease in sensor response to the use of more graphite compositions. Seen in the three types of graphite composition experienced the same increase during the increase in

formalin concentration, but the response level of the three sensors decreased with increasing graphite composition.

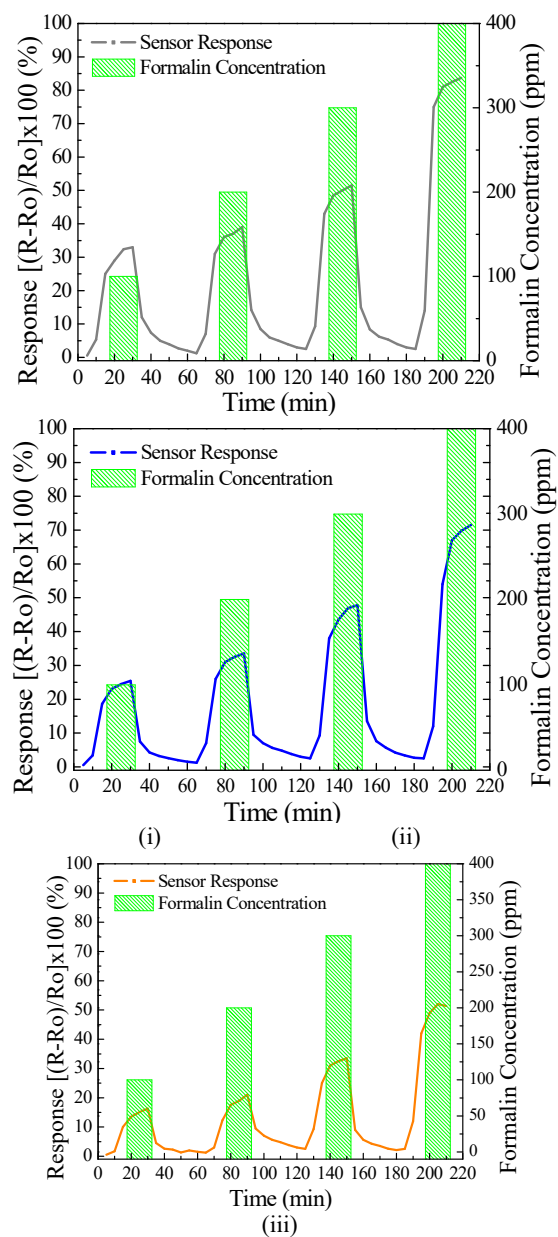


Figure 5. Sensor response to time with Graphite composition (i) 3%, (ii) 10% and (iii) 25%.

Extrapolating the data in Figure 6 shows the decrease of response sensor when used larger graphite composition. The formalin concentration of 100 ppm, was decreased the response by 7.6% in PANI|Graphite 10% and 16.7% in PANI|Graphite 25% compared to PANI|Graphite 3%. On the other hand, at formalin concentration of 400 ppm, the sensor response with 3% graphite showed a value of 1.62 times greater than the sensor with a graphite composition of 25%.

It is known that graphite promotes a better configuration for sensor devices, especially polyaniline [11]. The reason for achieving better results using graphite is related to improvements in the transfer of charge between polymers, graphite, and electrodes [1, 4]. In one study, the addition of graphite made electrical conductivity increase by 5 times compared to pure PANI, because of better transfer of charge between PANI and graphite [6, 7] But in this study, the performance of the sensor should not be assessed as the amount of conductivity. Because the addition of graphite is too much, the PANI absorption area becomes less because it was covered by the graphite [14]. The sensor indeed works as a condensation reaction for the formation of a Schiff base between amines in PANI and formalin. Sensor performance remains stable and good, but the measured resistance looks smaller because the sensor conductivity level is more dominated by graphite compared to PANI [15].

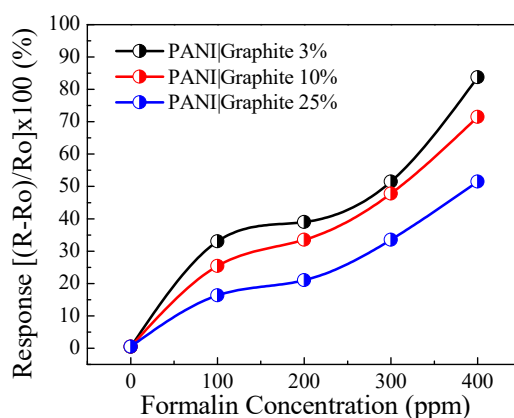


Figure 6. Sensor response to formalin concentration in PANI|Graphite.

The performance of the sensor was quite good at working at the formalin concentration of 100-400 ppm. The team has tried measuring below the concentration of the formalin, but the change in resistance is not enough if only used an Avometer. But the hope of researchers, through these results was used of the wider community will be more flexible, close to accurate, and accessible. Therefore, composites of polyaniline and graphite can be used as sensors to detect the presence of formaldehyde gas.

CONCLUSION

From the total concentration of formalin gas tested, the sensor with a graphite composition of 25% showed a considerable decrease in response. But all sensors still provide stable performance in the composition of 3%, 10%, or 25%. The addition of too much graphite makes the absorption area of PANI less because it is covered by the graphite. In this case, the performance of the sensor remains stable and good, but the measured resistance looks smaller because the level of conductivity of the sensor is more dominated by graphite compared to

PANI. The performance of the sensor is quite good at working at the formalin concentration of 100-400 ppm. Therefore, composites of polyaniline and graphite can be used as sensors to detect the presence of formaldehyde gas.

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